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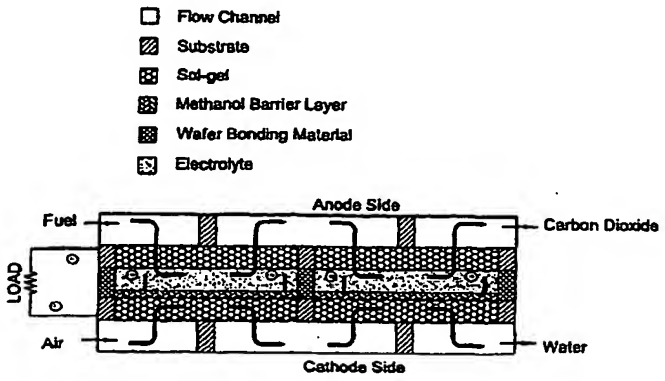

(57) Abstract: Fuel cell systems, electrode assemblies and electrode structure are disclosed herein. In one embodiment, the present invention is directed to an electrode assembly adapted for use with a fuel cell system, comprising: an anode derived from a first silicon substrate (with an optional sol-gel region); an electrolyte; and a cathode derived from a second silicon substrate (with an optional sol-gel region); wherein the anode and the cathode are spaced apart and substantially parallel to each other so as to define a spaced apart region, and wherein the electrolyte is interposed between the anode and the cathode, and wherein at least (i) the anode comprises one or more discrete anodic porous regions disposed across a top surface of the anode, wherein each of the one or more discrete anodic porous regions is defined by a plurality of anodic acicular pores that extend through the anode, and wherein the plurality of anodic acicular pores define inner anodic pore surfaces, or (ii) the cathode comprises one or more discrete cathodic porous regions disposed across a top surface of the cathode, wherein each of the one or more discrete porous cathodic porous regions is defined by a plurality of cathodic acicular pores that extend through the cathode, and wherein the plurality of cathodic acicular pores define inner cathodic pore surfaces.

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POROUS SILICON AND SOL-GEL DERIVED ELECTRODE STRUCTURES AND ASSEMBLIES ADAPTED FOR USE WITH FUEL CELL SYSTEMS

TECHNICAL FIELD

The present invention relates generally to fuel cell systems and, more specifically, to porous silicon and sol-gel derived fuel cell electrode structures and assemblies adapted for use with fuel cell systems.

BACKGROUND OF THE INVENTION

A fuel cell is an energy conversion device that consists essentially of two opposing electrodes, an anode and a cathode, ionically connected together via an interposing electrolyte. Unlike a battery, fuel cell reactants are supplied externally rather than internally. Fuel cells operate by converting fuels, such as hydrogen or a hydrocarbon (*e.g.*, methanol), to electrical power through an electrochemical process rather than combustion. It does so by harnessing the electrons released from controlled oxidation-reduction reactions occurring on the surface of a catalyst. A fuel cell can produce electricity continuously so long as fuel is supplied from an outside source.

In electrochemical fuel cells employing methanol as the fuel supplied to the anode (also commonly referred to as a "Direct Methanol Fuel Cell (DMFC)" system), the electrochemical reactions are essentially as follows: first, a methanol molecule's carbon-hydrogen, and oxygen-hydrogen bonds are broken to generate electrons and protons; simultaneously, a water molecule's oxygen-hydrogen bond is also broken to generate an additional electron and proton. The carbon from the methanol and the oxygen from the water combine to form carbon dioxide. Oxygen from air (supplied to the cathode) is likewise simultaneously reduced at the cathode. The ions (protons) formed at the anode migrate through the interposing electrolyte and combine with the oxygen at the cathode to form water. From a molecular perspective, the electrochemical reactions occurring within a direct methanol fuel cell (DMFC) system are as follows:

Anode:	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$	$E_0 = 0.04V$	*vs.* NHE	(1)
Cathode:	$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$E_0 = 1.23V$	*vs.* NHE	(2)
Net:	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2$	$E_0 = 1.24V$	*vs.* NHE	(3)

The various electrochemical reactions associated with other state-of-the-art fuel cell systems (*e.g.*, hydrogen or carbonaceous fuel) are likewise well known to those skilled in the art of fuel cell technologies.

With respect to state-of-the-art fuel cell systems generally, several different configurations and structures have been contemplated - most of which are still undergoing further research and development. In this regard, existing fuel cell systems are typically classified based on one or more criteria, such as, for example: (1) the type of fuel and/or oxidant used by the system, (2) the type of electrolyte used in the electrode stack assembly, (3) the steady-state operating temperature of the electrode stack assembly, (4) whether the fuel is processed outside (external reforming) or inside (internal reforming) the electrode stack assembly, and (5) whether the reactants are fed to the cells by internal manifolds (direct feed) or external manifolds (indirect feed). In general, however, it is perhaps most customary to classify existing fuel cell systems by the type of electrolyte (*i.e.*, ion conducting media) employed within the electrode stack assembly. Accordingly, most state-of-the-art fuel cell systems have been classified into one of the following known groups:

1. Alkaline fuel cells (*e.g.*, KOH electrolyte);
2. Acid fuel cells (*e.g.*, phosphoric acid electrolyte);
3. Molten carbonate fuel cells (*e.g.*, Li_2CO_3/K_2CO_3 electrolyte);
4. Solid oxide fuel cells (*e.g.*, yttria-stabilized zirconia electrolyte);
5. Proton exchange membrane fuel cells (*e.g.*, NAFION electrolyte).

Although these state-of-the-art fuel cell systems are known to have many diverse structural and operational characteristics, such systems nevertheless share many common characteristics with respect to their electrode structures. For example, one type of common electrode structures consists essentially of a conductive substrate (*e.g.*, metal plate or porous carbon-fiber sheet) that has a substantially planar catalytic

film/layer thereon (*e.g.*, affixed or embedded catalysts particles). Another type of electrode structure consists essentially of a porous bulk matrix substrate (*e.g.*, silicon and/or sol-gel) that has catalyst particles chemisorbed on the pore surfaces (*see, e.g.*, International Publication No. WO 01/37357, which publication is incorporated herein by reference in its entirety). Some of the problems associated with existing porous electrode structures include, for example: (1) poor catalyst utilization, (2) less than optimal electrical conductivity, and (3) mass transfer limitations associated with reactants reaching catalytic electrode surfaces. Thus, there is still a need in the art for improved fuel cell electrode structures, assemblies, and systems. The present invention fulfills these needs and provides for further related advantages.

SUMMARY OF THE INVENTION

In brief, the present invention relates generally to fuel cell systems and, more specifically, to porous silicon and sol-gel derived fuel cell electrode structures and assemblies adapted for use with fuel cell systems. In one embodiment, the present invention is directed to an electrode assembly adapted for use with a fuel cell system, comprising: an anode derived from a first silicon substrate (with an optional sol-gel region); an electrolyte; and a cathode derived from a second silicon substrate (with an optional sol-gel region); wherein the anode and the cathode are spaced apart and substantially parallel to each other so as to define a spaced apart region, and wherein the electrolyte is interposed between the anode and the cathode, and wherein at least (i) the anode comprises one or more discrete anodic porous regions disposed across a top surface of the anode, wherein each of the one or more discrete anodic porous regions is defined by a plurality of anodic acicular pores that extend through the anode, and wherein the plurality of anodic acicular pores define inner anodic pore surfaces, or (ii) the cathode comprises one or more discrete cathodic porous regions disposed across a top surface of the cathode, wherein each of the one or more discrete porous cathodic porous regions is defined by a plurality of cathodic acicular pores that extend through the cathode, and wherein the plurality of cathodic acicular pores define inner cathodic pore surfaces.

The fuel cell systems of the present invention may be gaseous or direct liquid feed fuel cell systems such as, for example, a direct methanol fuel cell system. In some embodiments, a flowing fluid reactant/electrolyte may ionically connect the anode to the cathode, wherein suitable fluid reactant/electrolytes include, for example, an organic liquid fuel combined with an acid solution (*i.e.*, a liquid aprotic organic electrolyte). Exemplary organic fuels comprise water and an alcohol such as ethanol, propanol, methanol, or a combination thereof; and the acid solution may be phosphoric acid, sulfuric acid, trifluoromethane sulfonic acid, or a combination thereof.

These and other aspects of the present invention will become more evident upon reference to the following detailed description and attached drawings. It is to be understood, however, that various changes, alterations, and substitutions may be made to the specific fuel cell electrode structures disclosed herein without departing from the essential spirit and scope of the present invention. In addition, it is to be further understood that the drawings are illustrative and symbolic representations of exemplary embodiments of the present invention (hence, they are not necessarily to scale). Finally, it is expressly provided that all of the various references cited herein are incorporated by reference in their entireties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a fuel cell system in accordance with the prior art.

Figure 2A illustrates a top plan view of an electrode structure having a plurality of acicular pores in accordance with an embodiment of the present invention.

Figure 2B illustrates a cross-sectional view of the electrode structure of Figure 2A, wherein the view is taken along line B-B of Figure 2A.

Figure 2C illustrates a top perspective view of the electrode structure of Figures 2A and 2B.

Figure 3A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention, wherein a planar anode and a planar cathode have porous silicon substrate regions, and wherein the planar anode and the planar cathode are attached to each other by a plurality of bridge members that span across a spaced apart region.

Figure 3B illustrates a top view of the electrode assembly of Figure 3A.

Figure 4A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 4B illustrates a top view of the electrode assembly of Figure 4A.

Figure 5A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention, wherein a planar anode and a planar cathode have sol-gel derived support structure regions, and wherein the planar anode and the planar cathode are attached to each other by a plurality of bridge members that span across a spaced apart region.

Figure 5B illustrates a top view of the electrode assembly of Figure 5A.

Figure 6A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 6B illustrates a top view of the electrode assembly of Figure 6A.

Figure 7A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 7B illustrates a top view of the electrode assembly of Figure 7A.

Figure 8A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 8B illustrates a top view of the electrode assembly of Figure 8A.

Figure 9A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 9B illustrates a top view of the electrode assembly of Figure 9A.

Figure 10A illustrates a cross-sectional view of an exemplary electrode assembly in accordance with an embodiment of the present invention.

Figure 10B illustrates a top view of the electrode assembly of Figure 10A.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates generally to fuel cell systems and, more specifically, to porous silicon and sol-gel derived fuel cell electrode structures and assemblies adapted for use with fuel cell systems. As is appreciated by those skilled in

the fuel cell technology art, a fuel cell system generally comprises a stack of electrode assemblies (referred to as an electrode stack assembly), wherein each individual electrode assembly consists essentially of two opposing electrode structures, an anode and a cathode, ionically connected together via an interposing electrolyte. The electrode stack assembly of such fuel cell systems also generally includes a series of flow channels for flowing reactant streams adjacent to and/or through discrete regions of the electrode structures. A fuel cell system in accordance with the prior art is shown in Figure 1 (structural details have been omitted).

In the several embodiments set forth herein, the inventive fuel cell systems, electrode assemblies, and electrode structures are based, in large part, on novel substrates and support structures that are particularly useful for carrying a catalyst, wherein the catalyst is readily accessible to flowing gaseous and/or liquid reactant streams. In this regard, the substrate and support structures disclosed herein principally include silicon substrates, sol-gel derived support structures, and combinations thereof. In particular, it has been discovered that these types of substrates and/or support structures are particularly useful as electrodes for fuel cell systems (especially for micro-scale direct methanol fuel cell systems), mainly because such substrates and/or support structures are able to provide a high surface area to bulk volume ratio, have good mechanical strength, and are compatible with thin/thick films that are often need for making selected electrical connections. Because of these physical characteristic, among others, and because such substrates and/or support structures are amenable to micro-fabrication techniques, the electrode structures, electrode assemblies, and fuel cell systems of the present invention are useful for the manufacture of small-scale portable power generating devices - portable power devices capable of delivering up to 200 Watts of power.

Accordingly, and without limitation to any particular methodology, the novel silicon substrates disclosed herein may be made by utilizing standard microelectronic processes such as, for example, alkaline etching, plasma etching, lithography, electroplating, as well as electrochemical pore formation on silicon substrates and wafers. In this way, a silicon substrate useful for carrying a catalyst may be produced, wherein the silicon substrate may have any number of pores and pores

sizes such as, for example, random or ordered pore arrays - including pore arrays having selected pore diameters, depths, and distances relative to one another. Similarly, the novel sol-gel derived support structures may be made by conventional sol-gel processing techniques, wherein the sol-gel derived support structures may have any number of pores, pores sizes, and/or pore structures. In short, the present invention is inclusive of all silicon substrates and sol-gel derived support structures, including combinations thereof, that have any number of possible porosities and/or void spaces associated therewith.

An exemplary embodiment of a porous silicon electrode structure of the present invention is shown in Figures 2A-C, which drawings show an isolated electrode structure 200 (which structure is adapted for use with a fuel cell system). The electrode structure 200 comprises a silicon substrate 210 (thickness ranging from about 300 to about 500 microns) having one or more discrete porous regions 220 disposed across a top surface 230 of the substrate 210. In addition, each of the one or more discrete porous regions 220 is defined by a plurality of acicular or columnar pores 240 that extend through the substrate 210 (diameter ranging from about 0.5 to about 10 microns). The plurality of acicular or columnar pores define inner pore surfaces 250, and the inner pore surfaces 250 may have an optional conformal electrically conductive layer 270 thereon. In some embodiments and as shown, the pores are substantially perpendicular to the top and bottom surfaces 230, 235 of the substrate 210. In some other embodiments, the pores each have a diameter of about 10 microns and are spaced apart from one another about 10 microns (from pore center axis to adjacent pore center axis) so as to yield substrate having an approximate 39% porosity.

Porous silicon substrates (and/or support structures) useful as electrode structures may be formed by silicon micro-machining and/or wet chemical techniques (employed by the semiconductor industry) such as, for example, anodic polarization of silicon in hydrofluoric acid. As is appreciated by those skilled in the art, the anodic polarization of silicon in hydrofluoric acid (HF) is a chemical dissolution technique and is generally referred to as HF anodic etching; this technique has been used in the semiconductor industry for wafer thinning, polishing, and the manufacture of thick porous silicon films. (*See, e.g.,* Eijkel, et al., "A New Technology for Micromachining

of Silicon: Dopant Selective HF Anodic Etching for the Realization of Low-Doped Monocrystalline Silicon Structures," *IEEE Electron Device Ltrs.*, *11*(12):588-589 (1990)). In the context of the present invention, it is to be understood that the porous silicon may be microporous silicon (*i.e.*, average pore size < 2 nm), mesoporous silicon (*i.e.*, average pore size of 2 nm to 50 nm), or microporous silicon (*i.e.*, average pore size > 50 nm); the pores may also be a series of parallelly aligned acicular or columnar pores that extend into or through the silicon substrate. Although the pores may be angled, they are preferably substantially perpendicular to the surfaces of the substrate.

More specifically, porous silicon substrates useful in the context of the present invention may be formed by a photoelectrochemical HF anodic etching technique, wherein selected oxidation-dissolution of silicon occurs under a controlled current density. (*See, e.g.*, Levy-Clement et al., "Porous n-silicon Produced by Photoelectrochemical Etching," *Applied Surface Science*, *65/66*: 408-414 (1993); M.J. Eddowes, "Photoelectrochemical Etching of Three-Dimensional Structures in Silicon," *J. of Electrochem. Soc.*, *137*(11):3514-3516 (1990).) An advantage of this relatively more sophisticated technique over others is that it is largely independent of the different principal crystallographic planes associated with single-crystal silicon wafers (whereas most anisotropic wet chemical etching methods have very significant differences in rates of etching along the different principal crystallographic planes).

In the context of the present invention, an electrode assembly adapted for use with a fuel cell system generally comprises: an anode derived from a first silicon substrate, an electrolyte, and a cathode derived from a second silicon substrate. The anode is generally processed so as to have one or more discrete anodic porous regions disposed across a top surface of the anode, wherein each of the one or more discrete anodic porous regions is defined by a plurality of anodic acicular pores that extend through the anode, and wherein the plurality of anodic acicular pores define inner anodic pore surfaces. Similarly, the cathode is generally processed so as to have one or more discrete cathodic porous regions disposed across a top surface of the cathode, wherein each of the one or more discrete porous cathodic porous regions is defined by a plurality of cathodic acicular pores that extend through the cathode, and wherein the plurality of cathodic acicular pores define inner cathodic pore surfaces. The anode and

cathode are generally spaced apart and substantially parallel to each other so as to define a spaced apart region, and the electrolyte is generally interposed between the anode and the cathode.

In addition, the electrode assembly may further comprise a fluid delivery channel disposed across a first face of the anode or the cathode; and a fluid removal channel disposed across a second face of the anode or the cathode; wherein at least one of the one or more discrete anodic porous regions or at least one of the one or more discrete cathodic porous regions is (i) interposed between the fluid delivery channel and the fluid removal channel, and (ii) adapted to flow a liquid therebetween (*e.g.*, the acicular or columnar pores serve as hydrodynamic transport channels or fluid flow through-holes). In such a configuration, a solid polymer electrolyte (*e.g.*, NAFION, E.I DuPont de Nemours, United States) or a flowing fluid reactant/electrolyte may ionically connect the anode to the cathode. In the context of the present invention, suitable fluid reactant/electrolytes include, for example, an organic liquid fuel combined with an acid solution (*i.e.*, a liquid aprotic organic electrolyte). Exemplary organic fuels comprise water and an alcohol such as ethanol, propanol, methanol, or a combination thereof; and the acid solution may be phosphoric acid, sulfuric acid, trifluoromethane sulfonic acid, or a combination thereof. In some embodiments, the fluid reactant/electrolyte comprises equal molar amounts of methanol and water together with an acid in an amount of about 0.01 to 3.0 M, and preferably in an amount of about 0.25 M. Exemplary fluid delivery channels and flowing fluid reactant/electrolyte schemes associated with the present invention as shown in Figures 3A through 10B.

Thus, and in accordance with the embodiment represented by Figures 3A and 3B, the present invention is directed to an electrode assembly 300 that comprises a planar anode 302 made from a silicon substrate, an electrolyte layer 304, a planar cathode 306 made from a silicon substrate, and optionally a blocking layer 308 that is substantially impermeable to at least methanol and is substantially permeable to protons. As shown, the planar anode 302 and the planar cathode 306 are spaced apart and substantially parallel to each other so as to define a spaced apart region 310, wherein the electrolyte layer 304 and optional blocking layer 308 are interposed between the planar anode 302 and the planar cathode 306 and within at least a portion

of the spaced apart region 310, and wherein the planar anode 302 and the planar cathode 306 are attached to each other by at least one bridge member 312 that spans across the spaced apart region 310. As depicted, fuel (optionally combined with a liquid electrolyte) flows through the anode and, in some embodiments, through the spaced apart region 310; an oxidant such as, for example, air, oxygen, or a hydrogen peroxide solution simultaneously flows through the cathode. Other exemplary electrode assemblies in accordance with the present invention are depicted in Figures 4A through 10B.

The electrode assembly may still further comprise a conformal electrically conductive layer on at least one of the inner anodic pore surfaces or inner cathodic pore surfaces. More specifically, the conformal electrically conductive layer of the present invention may be selectively deposited on the one or more pore surfaces of the selected substrate (*i.e.*, porous silicon and/or sol-gel derived support structure) by use of a sequential gas phase deposition technique such as, for example, atomic layer deposition (ALD) or atomic layer epitaxy (ALE). As with more traditional chemical vapor deposition (CVD) techniques, the reactants or precursors used with a sequential atomic deposition technique are introduced into a deposition or reaction chamber as gases. Unlike CVD, however, the reactants or precursors used are supplied in pulses, separated from each other (in the flow stream) by an intervening purge gas. Each reactant pulse chemically reacts with the substrate; and it is the chemical reactions between the reactants and the surface that makes sequential atomic deposition a self-limiting process that is inherently capable of achieving precise monolayer growth (*see, e.g., Atomic Layer Deposition,* T. Suntola and M. Simpson, Eds., Blackie and Sons (1990)).

In this regard, solid thin films may be grown on heated substrates by exposing the heated substrate to a first evaporated gaseous element or compound, allowing a monolayer of the element to form on the surface of the substrate, and then removing the excess gas by evacuating the chamber with a vacuum pump (or by use of a purge gas such as Argon or Nitrogen). Next, a second evaporated gaseous element or compound may be introduced into the reaction chamber. The first and second elements/compounds can then combine to produce a solid thin compound monolayer

film. Once the monolayer film has been formed, any excess second evaporated gaseous element or compound may be removed by again evacuating the chamber with the vacuum pump. The desired film thickness may be built up by repeating the process cycle many (*e.g.*, hundreds or thousands) of times. Accordingly, such an atomic deposition technique may be used to deposit on an electrode support structure (*e.g.*, silicon or other appropriately selected substrate) a variety of materials, including group II-VI and III-V compound semiconductors, elemental silicon, SiO_2, and various metal oxides and nitrides thereof. In one preferred embodiment, however, an atomic layer deposition (ALD) technique is used to selectively deposit on the pore surfaces of a porous silicon support structure a conformal electrically conductive layer that consists essentially of a first tungsten or ruthenium layer (about 2,000 Å thick) together with a second platinum layer (about 100 Å thick). The conformal electrically conductive layer enhances electrical conductivity (between the electrons released on the catalyst as a result of electrochemical oxidation-reduction reactions), and also functions as a catalyst.

Moreover, and as noted above, atomic deposition techniques may also be used to deposit a film or layer containing a metal and a non-metal such as, for example, O or N. In such a scenario, the first reactant pulse may contain the metal and the second reactant pulse the non-metal. The first pulse deposits a metal-containing layer, and the reactant of the second pulse reacts with that layer to form the complete film of metal oxide or metal nitride. Both reactants react chemically with the surface on which they deposit, and each reaction is self-limiting. In this way, film or layer thicknesses may be controlled to within a monolayer solely by limiting the number of pulses. In addition to being extremely uniform and conformal, the deposited films may be amorphous, epitaxial or polycrystalline. In the context of the present invention, the deposition rate of the atomic deposition process is preferably about one atomic layer and the reaction temperature is preferably ranges from about 200-400°C.

In further embodiments of the present invention, the conformal electrically conductive layer may have deposited thereon a plurality of catalysts particles such as, for example, bi-metallic particles of platinum and ruthenium (*i.e.*, chemisorbed bi-metallic catalysts particles derived from platinum and ruthenium precursors). Thus, a noncontiguous bi-metallic layer of platinum and ruthenium may be

chemisorbed on the exposed surfaces of the conformal electrically conductive layer by selective use of platinum and ruthenium precursors. For example, a conformally coated porous silicon substrate may be immersed, under basic conditions (pH 8.5), into an aqueous ammonia solution of tetraamineplatinum(II) hydroxide hydrate, $[Pt(NH_3)_4](OH)_2$-xH_2O, and stirred for a selected period of time. The various precursors listed above are generally available from Strem Chemicals, Inc., Newburyport, Maine.

In addition to such wet chemical techniques, noncontiguous layers may also be formed by the above described sequential atomic deposition techniques, wherein such layers comprise either islands of nanocrystallites or an interconnected network of nanocrystallites. In this regard, island formation may be controlled to some degree by increasing or decreasing the number of bonding sites on the surface of the underlying substrate or support structure. For example, metal concentration on the surface may be decreased by reducing the number of bonding sites by either dehydroxylation (heat treatment) or chemical blocking of the bonding sites with, for example, hexamethyldisilazane (HMDS) (E. Lakomaa, "Atomic Layer Epitaxy (ALE) on Porous Substrates," *J. Applied Surface Science 75*:185-196 (1994)).

In still further embodiments, the electrode assembly further comprises a metallic blocking layer that is (1) integrally associated with either the anode or cathode, and (2) interposed between the anode and cathode. The metallic blocking layer is generally a substantially voidless metallic membrane that is substantially impermeable to at least methanol and is substantially permeable to hydrogen atoms. Accordingly, the metallic blocking layer is preferably a palladium thin film adhered to either the anode or cathode, wherein the blocking layer has a thickness of about 1 to 5 microns (blocking layer thickness depends upon pore diameter; smaller pore diameters may support thinner films). The blocking layer, however, may comprise palladium, niobium, tantalum, vanadium, or a combination thereof. As is appreciated by those skilled in the art, such thin films may be deposited so as to cover a porous surface by, for example, electroplating, physical vapor deposition, sputtering, thermal evaporation, e-beam evaporation, or electroless deposition.

Another aspect of the present invention relates to a porous silicon electrode structure that has been selectively doped so as to form one or more selectively doped regions. The doped regions are each adapted to function as a current collector for the transmission of an electrical current. As is appreciated by those skilled in the art, silicon may be selectively doped (via appropriate masking of the silicon substrate) by high-temperature diffusion and/or ion implantation. Boron is preferably used as a p-type dopant whereas antimony, phosphorous, and arsenic may be used as *n*-type dopants. However, because doping may adversely affect the HF anodic etching process (tends to mess up the pore morphology), it is generally preferable to selectively dope the silicon substrates of the present invention after the porous regions have been formed. In this way, the porous regions and surrounding interconnect channels may be made more conductive to electron transport, thereby facilitating electrical current removal and delivery to an outside source.

In still further embodiments, the present invention utilizes an electrode made with a sol-gel derived support structure (optionally integrated together with a silicon substrate). As is appreciated by those skilled in the art, sol-gel processes are a way to make dispersed ceramic materials through the growth of metal oxo polymers in a solvent. (*see, e.g.,* Brinker et al., "Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing," *Academic* (1990).) The chemistry associated with sol-gel processes is based on inorganic polymerization reactions. In this regard, metal oxo polymers may be obtained through hydrolysis and condensation of molecular precursors such as metal alkoxides M(OR)z (wherein M = Si, Ti, Al, Zr, V, W, Ir, Mn, Mo, Re, Rh, Nb, Ni, Sr, Ba, Ta, Mg, Co; OR is an alkoxy group and Z is the valence or oxidation state of the metal) (Sanchez et al., "Inorganic and Organometallic Polymers with Special Properties," *Nato ASI Series* (Laine R. M., Ed.), *206*:267 (1992)). The mechanism occurs in three steps: (a) nucleophilic attack of the metal M by an oxygen atom of a water molecule; (b) transfer of a proton from the water to an OR group of the metal; and (c) release of the resulting ROH molecule (Livage et al., "sol-Gel Chemistry of Transition-Metal Oxides," *Progress in Solid State Chemistry,* 18(4):259-341 (1988)). As soon as reactive hydroxy groups are generated, the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy

groups occurs through a polycondensation process. Depending upon experimental conditions, two competitive mechanism have been described, namely, oxolation and olation. In exemplary embodiments of the present invention, a sol-gel derived support structure may be cast into etched or micromachined trenches, channels, and/or pits of a silicon substrate (*e.g.*, a silicon wafer with selectively placed trenches), wherein the sol-gel derived support structure combined with the silicon substrate (together with a catalyst) serves as an electrode of a fuel cell system.

In an exemplary embodiment of the present invention, a sol-gel derived support structure comprising platinum ruthenium dioxide (Pt-RuO_2) may be cast into etched or micromachined trenches, channels, and/or pits of a silicon substrate, wherein the sol-gel derived support structure combined with silicon substrate and a catalyst serves as an electrode of a fuel cell. An exemplary platinum-ruthenium oxide precursor solution useful for this purpose may be prepared, for example, by mixing hexachloroplatinic acid (H_2PtCl_6 xH_2O), ruthenium nitrosyl nitrate ($Ru(NO)(NO_3)_x(OH)_{3-x}$) with nitric acid (HNO_3), ethyl alchohol (C_2H_5OH), and DI water. The solution may be refluxed under vigorous stirring at ~ 60°C for ~ 1 hr to yield a nominal molar ratio of 1 : 0.5 : 5 : 0.08 : 20 of H_2PtCl_6 xH_2O : $Ru(NO)(NO_3)_x(OH)_{3-x}$: H_2O : HNO_3 : C_2H_5OH. (Chemicals are commercially available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.)

Alternatively, an exemplary ruthenium dioxide precursor solution may be prepared, for example, by dissolving ruthenium chloride hydrate $RuCl_3$ XH_2O) in a mixture of ethyl alcohol, nitric acid, and DI water. The solution may be refluxed under vigorous stirring at ~ 60°C for ~ 1 hr to yield a nominal molar ratio of 1 : 20 : 5 : 0.08 of RuCl3Xh20 : C_2H_5OH : H_2O : HNO_3 (optionally, a 10 wt% ruthenium (IV) oxide submicron particles may then be dispersed into the precursor solution). (Chemicals are commercially available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.)

Alternatively, an exemplary aluminum oxide precursor solution may be prepared by mixing aluminum sec-butoxide ($Al[O(CH_3)CHC_2H_5]_3$), hydrochloric acid (HCl), ethyl alcohol (C_2H_5OH), and DI water. The solution may be refluxed under vigorous stirring at ~ 60°C ~ 1 hr to yield a nominal molar ratio of 1 : 0.5 : 20 : 40 of

$Al[O(CH_3)CHC_2H_5]_3$: HCl : C_2H_5OH : H_2O. (Chemicals are commercially available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.)

Alternatively, an exemplary vanadium pentoxide precursor solution may be prepared by mixing vanadyl triisopropoxide ($VO(OC_3H_7)_3$), ethyl alcohol (C_2H_5OH), and DI water. The solution will be refluxed under vigorous stirring at ~ 60°C for ~ 1hr to yield a nominal molar ration of 1 : 15 : 30 of $VO(OC_3H_7)_3$: CH_3OCH_3 : H_2O. (Chemicals are commercially available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.)

For purposes of illustration and not limitation, the following examples more specifically disclose various aspects of the present invention.

EXAMPLES

Examples 1-4 disclose, among other, methodologies for generating porous silicon substrate, where as Examples 5-10 disclose, among other things, general processing steps associated with making an electrode structure for use with a fuel cell system, wherein the electrode structure comprises a silicon substrate having a plurality of acicular or columnar pores that extend through the substrate, wherein each of the plurality of pores has one or more atomic layers of an electrically conductive material deposited thereon. In some of these examples, Ru and RuO_2 precursors are used in an ALD process to derive an electrode structure in accordance with certain embodiments of the present invention.

EXAMPLE 1

RECIPE FOR 10 MICRON PORES W/ 10 MICRON PITCH, 35% POROSITY

The silicon sample was pre-structured; KOH etched 10-micron diameter pits for pore initiation. It was a N-type silicon with resistivity of 100 ohm-cm, (100) crystal orientation and 525-micron thickness, the silicon sample was etched in 3 wt%HF-H2O solution with an additional 100 ml of ethanol at a current density of 1.00 mA/cm^2. A potential of 6 volts was also applied. For the above sample, the etching time was done for about 3 hours. The resulting acicular or columnar pores were

perpendicular into the wafer with an average depth of 150 microns. Deeper pores may be obtained with longer etches. A typical membrane with acicular or columnar through holes would require about 24 hours etching (~500 microns). The final porous silicon membrane with acicular or columnar through holes was then made by grinding off the remaining 100 microns of silicon. Each pore was roughly 10 microns in diameter, which translates to about a 35% membrane porosity.

EXAMPLE 2

RECIPE FOR 5 MICRON PORES W/ 3, 4 AND 7 MICRON PITCH, 39% POROSITY

N-type silicon with resistivity of 23-27 ohm-cm, (100) crystal orientation and 525-micron thickness, the silicon sample was etched in 4 wt%HF-H2O solution with an additional 1 vol% (of the HF solution) surfactant (NCW-1001) at a current density of 10.00 mA/cm^2. A potential of 1.4 volts was also applied. For the above sample, the etching time was done for about 5 hours. The resulting acicular or columnar pores were perpendicular into the wafer with an average depth of 150 microns. Deeper pores may be obtained with longer etches. A typical membrane with the above shown pores would require about 24 hours etching (~500 microns). Each acicular or columnar pore was roughly 5 microns in diameter. The porous membrane was of about 39% porosity.

EXAMPLE 3

RECIPE FOR RANDOMLY GENERATED PORES OF 1-3 MICRON DISTRIBUTION

The above porous silicon sample was generated with randomly distributed pores. The etching conditions were: 1.5 mA/cm^2 current density, 6 volts potentials and 20° C etching temperature. The sample was of (100) crystal orientation, n-type with resistivity of 1-10 ohm-cm and 525 micron thickness. The silicon sample was etched in 3 wt%HF-H2O solutions. A typical membrane with the above shown pores would require about 24 hours etching (~500 microns). Each pore was roughly 2 microns in diameter.

EXAMPLE 4

RECIPE FOR RANDOMLY GENERATED PORES OF 1-3 MICRON DISTRIBUTION WITH VARIED TOP LAYER POROUS SILICON LAYERS

(100) oriented n-type silicon of 1-10 ohm-cm resistivity at 525 micron thickness was initially anodically etched in one surface at 4 wt%HF-H2O electrolyte with 1 vol% NCW-1001 surfactant. The etching was done at 6 volts, 2 mA/cm^2 and at 20°C. The resulting acicular or columnar pores extended into each wafer with an average depth of 400 + microns. The through holes were created by etching the opposite surface of the silicon wafer at 10 wt%HF-H2O electrolyte with 1 vol% NCW-1001. The etching conditions were at 6 volts, 2 mA/cm^2 and at 20°C. The resulting membrane had a through hole consisting of wavy columnar pores having two distinct pore diameter ranges. The first ranged from about 2-3 microns while the other ranged from about 100 to about 500 nm pores.

EXAMPLE 5

ALD PROCESS STEPS FOR DEPOSITING RUTHENIUM ON POROUS SILICON

A Ruthenium precursor is selected from the group consisting of $Ru_3(CO)_{12}$ (Dodecacarbonyltriruthenium), $(C_{11}H_{19}O_2)_2(C_8H_{12})Ru$ (Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium (II)), and $[(CH_3CH_2)C_5H_4]_2Ru$ (Bis(ethylcyclopentadienyl)ruthenium (II)). The selected precursor is then thermostated at 100°C. Argon is used as both the precursor carrier and the purge gas at a pressure of 100 mtorr. An electrode structure that comprises a silicon wafer having a plurality of acicular pores is then introduced into the reaction chamber of a suitable ALD device; and its temperature is raised to between 150°C and 175°C. Alternating pulses of the precursor and the purge gas are then introduced into the reaction chamber, wherein the pulse duration of the selected precursor is about 1.0 second at 100 mtorr and the purge duration is about 2.0 seconds at 100 mtorr. The

number of alternating pulses selected determines the thickness of the one or more atomic layers deposited.

EXAMPLE 6

ALD PROCESS STEPS FOR DEPOSITING RUTHENIUM OXIDE ON POROUS SILICON

Essentially the same as above except that $Ru_3(CO)_{12}$ is selected as the precursor and O_2 is used. In this example, the $Ru_3(CO)_{12}$ precursor and O_2 are separately pulsed through the reaction chamber with intervening Argon purging steps. The substrate/growth temperature is set to between 120-150°C. The pulse duration is about 1.0 second for $Ru_3(CO)_{12}$ at 100 mtorr and about 1.0 second for O_2 at 300-400 mtorr, whereas the separating purging pulses of Argon at 100 mtorr are about 2.0 seconds in duration.

EXAMPLE 7

ALD PROCESS STEPS FOR BIMETALLIC ANODE CATALYST SYSTEM DEPOSITED ON POROUS SILICON HAVING PLATINUM NANOCRYSTALLITES AND AN UNDERLYING RUTHENIUM LAYER

A pure Ruthenium film is first deposited onto the porous silicon substrate in the following steps. A suitable Ruthenium precursor is thermostated between 100-250°C, which results in a vapor pressure of approximately 0.05-10 Torr. Oxygen gas or water vapor is used as a second precursor if Ruthenium oxide is to be deposited. Hydrogen gas is used as a second precursor if Ruthenium is to be deposited. Argon or Nitrogen is used as both the precursor carrier and the purge gas at a pressure between 0.1-0.5Torr. The substrate/growth temperature is varied between 100 and 300°C. A cycle generally consists of alternating pulses of the two precursors separated by pulses of the purge gas, the pulse duration of the precursors is 0.5-20 seconds and the purge duration is 15-30 seconds. Platinum nanocrystallites are subsequently deposited by limiting the number of reaction cycles to 100-200 cycles, yielding islands of platinum between 2-20nm in size. Each cycle consists of alternating pulses of the

selected platinum precursor and Hydrogen gas with durations of 0.5-20 seconds, separated by pulses of the purge gas with durations of 15-30 seconds.

EXAMPLE 8

ALD PROCESS STEPS FOR A CONFORMAL RUTHENIUM LAYER DEPOSITED ON PRE-TREATED POROUS SILICON

Poor coverage and non-uniformity has been observed in deposition of metallic films onto silicon and silicon oxide, also film growth has been observed to be restricted by interdiffusion and metal silicide formation (M. Utriainen, M. Kroger-Laukkanen, L.S. Johansson, L. Niinisto, "Studies of metallic thin film growth in an atomic layer epitaxy reactor using $M(acac)_2$ (M=Ni, Cu, Pt) precursors," *J. Appied Surface Scence. 157*:151-158 (2000)). A way to ensure conformal Ruthenium film growth and adhesion on silicon without silicide formation is by first depositing a layer of Ruthenium oxide onto pre-treated silicon substrate. The silicon substrate may be pre-treated by thermal oxidation at 300-400°C in air in order to provide a more stable surface for deposition of Ruthenium oxide. Exposure of the silicon substrate to water vapor could also increase the presence of reactive surface sites such as hydroxyl groups, thereby increasing the surface saturation or coverage of the metal precursor. The deposited Ruthenium oxide may then be reduced to pure metallic Ruthenium with Hydrogen gas or radicals. Subsequent Ruthenium may then be deposited by direct layer-by-layer reduction of an adsorbed Ruthenium precursor using Hydrogen gas or radicals to increase the overall film thickness and uniformity.

EXAMPLE 9

ALD PROCESS STEPS FOR DEPOSITION OF CATALYST NANOCRYSTALLITES:

Active catalyst surface area can be significantly increased by forming nanocrystallites of Platinum and Ruthenium instead of a continuous film. Although ALD growth theoretically should proceed in a layer-by-layer fashion, phenomena of island formation or nucleation of agglomerates during early stages of ALD growth have

been reported (T. Suntola, "Surface Chemistry of Materials Deposition at Atomic Layer Level," *J. Applied Surface Science 100/101*:391-398 (1996)). It is, therefore, possible to encourage island formation and thus growth of nanosize particles by controlling surface saturation density in three different ways. One way is to increase the size of the precursor molecule, in other words, choosing a Ruthenium and/or Platinum metal precursor with bulky ligands to increase the spacing between the resulting metal atoms thus reducing the metal density. One example of such a precursor is Bis (2,2,6,6-tetramethyl-3,5-heptanedionato) (1,5-cyclooctadiene) ruthenium (II), $Ru(C_{11}H_{19}O_2)_2(C_8H_{12})$. Another way is to regulate the number of bonding sites on the silicon substrate. It has been shown in studies (E.L. Lakomaa, "Atomic Layer Epitaxy (ALE) on Porous Substrates," *J. Applied Surface Science 75*:185-196 (1994)) that hydroxyl groups on the surface of metal oxides serve as bonding sites for metal chlorides and acetylacetonates and possibly other metal precursors - thus the number of these sites may be regulated by heat treatment before binding the active metal precursor. In our case, low metal surface density may be achieved by oxidizing the porous silicon substrate followed by exposure to water vapor to first generate surface hydroxyl groups, and then regulate the number of the surface hydroxyl groups by suitable heat treatment. A third way to control surface saturation density is to reduce the number of bonding sites by employing bulky organic precursor molecules such as HMDS to physically block potential binding sites (*e.g.*, hydroxyl groups). Suitable Ruthenium and Platinum precursors are, for example, Ruthenium (III) acetylacetonate, $Ru(CH_3COCHCOCH_3)_3$ and Platinum (II) acetylacetonate, $Pt(CH_3COCHCOCH_3)_2$. Additionally, substrate temperature may be increased to promote mobility of adsorbed metal atoms favoring nucleation and crystallization. Once the nanocrystallites are formed as islands, the number of cycles applied in a run should be limited so as to prevent crystallites/agglomerates from growing laterally into a continuous film (thereby forming an interconnected network of nanocrystallites).

EXAMPLE 10

ALD PROCESS STEPS FOR BIMETALLIC ANODE CATALYST SYSTEM DEPOSITED ON POROUS SILICON HAING PLATINUM AND RUTHENIUM ALLOY AND AN UNDERLYING RUTHENIUM LAYER

Catalyst activity and stability at the anode of a direct methanol fuel cell is a function of the Platinum to Ruthenium ratio. Therefore, it is important to be able to vary that ratio at the atomic level in a homogeneous manner. Concentrations of Platinum and Ruthenium may be adjusted accurately by mixing their respective inorganic salts in a mutual solvent. The homogeneous mixture may then be used as a single precursor to deposit an alloy of the two with the desired atomic ratio. For example, Ruthenium (III) Chloride and Dihydrogen hexachloroplatinate (IV) may be mixed and dissolved in ethanol and used as a single precursor in an atomic deposition process.

While the present invention has been described in the context of the embodiments illustrated and described herein, the invention may be embodied in other specific ways or in other specific forms without departing from its spirit or essential characteristics. Therefore, the described embodiments are to be considered in all respects as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

1. An electrode assembly adapted for use with a fuel cell system, comprising:

an anode derived from a first silicon substrate;

an electrolyte; and

a cathode derived from a second silicon substrate;

wherein the anode and the cathode are spaced apart and substantially parallel to each other so as to define a spaced apart region, and wherein the electrolyte is interposed between the anode and the cathode, and wherein at least (i) the anode comprises one or more discrete anodic porous regions disposed across a top surface of the anode, wherein each of the one or more discrete anodic porous regions is defined by a plurality of anodic acicular pores that extend through the anode, and wherein the plurality of anodic acicular pores define inner anodic pore surfaces, or (ii) the cathode comprises one or more discrete cathodic porous regions disposed across a top surface of the cathode, wherein each of the one or more discrete porous cathodic porous regions is defined by a plurality of cathodic acicular pores that extend through the cathode, and wherein the plurality of cathodic acicular pores define inner cathodic pore surfaces.

2. The electrode assembly of claim 1 wherein the fuel cell system is a direct liquid feed fuel cell system.

3. The electrode assembly of claim 2 wherein the direct liquid feed fuel cell system is direct methanol fuel cell system.

4. The electrode assembly of claim 1 wherein the electrolyte comprises an organic liquid fuel and a liquid aprotic organic electrolyte.

5. The electrode assembly of claim 4 wherein the organic liquid fuel is ethanol, propanol, methanol, or a combination thereof.

6. The electrode assembly of claim 4 wherein the liquid aprotic organic electrolyte is phosphoric acid, sulfuric acid, trifluoromethane sulfonic acid, or a combination thereof.

7. The electrode assembly of claim 1 wherein the plurality of anodic acicular pores and cathodic acicular pores have diameters ranging from about 0.5 to about 10 microns.

8. The electrode assembly of claim 1 wherein the anode and the cathode each have thicknesses ranging from about 300 to about 500 microns.

9. The electrode assembly of claim 1, further comprising a metallic blocking layer integrally associated with either the anode or the cathode, and wherein the metallic blocking layer is interposed between the anode and the cathode.

10. The electrode assembly of claim 7 wherein the metallic blocking layer is a substantially voidless metallic membrane that is substantially impermeable to at least methanol and is substantially permeable to hydrogen atoms.

11. The electrode assembly of claim 7 wherein the metallic blocking layer has thickness ranging from about 1 to 5 microns.

12. The electrode assembly of claim 8 wherein the metallic blocking layer comprises palladium.

13. The electrode assembly of claim 1 or 7 wherein at least the anode or the cathode has been selectively doped to define one or more selectively doped regions.

14. The electrode assembly of claim 1 or 7 wherein at least the anode or the cathode comprises a sol-gel.

15. The electrode assembly of claim 12 wherein the sol-gel comprises platinum ruthenium dioxide, platinum-ruthenium-silicon oxide, platinum-ruthenium-titanium oxide, platinum-ruthenium-zirconium oxide, platinum-ruthenium-aluminum oxide, or a combination thereof.

16. The electrode assembly of claim 12 wherein the sol-gel consist essentially of platinum ruthenium dioxide.

17. The electrode assembly of claim 1 or 7 wherein at least the anode or the cathode comprises:

a fluid delivery channel disposed across a first face of the anode or the cathode; and

a fluid removal channel disposed across a second face of the anode or the cathode;

wherein at least one of the one or more discrete anodic porous regions or at least one of the one or more discrete cathodic porous regions is (i) interposed between the fluid delivery channel and the fluid removal channel, and (ii) adapted to flow a liquid therebetween.

18. The electrode assembly of claim 1, further comprising a conformal electrically conductive layer on at least one of the inner anodic pore surfaces or inner cathodic pore surfaces.

19. The electrode structure of claim 16 wherein the conformal electrically conductive layer consists essentially of one or more atomic deposition layers, wherein the one or more atomic deposition layers are formed by an atomic layer deposition technique.

20. The electrode structure of claim 16 wherein the conformal electrically conductive layer consists essentially of Ag, Au, C, Cu, Mo, N, Nb, Ni, O, Pt, Pd, Ru, Rh, Re, Ta, Ti, W or a combination thereof.

21. The electrode structure of claim 16 wherein the conformal electrically conductive layer consists essentially of a first tungsten or ruthenium layer together with a second platinum layer.

22. The electrode structure of claim 16 wherein the conformal electrically conductive layer has a thickness ranging from about 500 to about 2,500 Å.

23. The electrode structure of claim 16 wherein the conformal electrically conductive layers has an electrical resistivity ranging from about 2.0 mΩ-cm to about 1,000 mΩ-cm.

24. The electrode structure of claim 16, further comprising a plurality of catalyst particles dispersed across a surface of the conformal electrically conductive layer.

25. The electrode structure of claim 22 wherein the plurality of catalyst particles are chemisorbed bi-metallic particles derived from platinum and ruthenium precursors.

26. The electrode structure of claim 1, further comprising a plurality of catalyst particles dispersed across at least (i) the inner anodic pore surfaces, or (ii) the cathodic pore surfaces.

27. The electrode structure of claim 24 wherein the plurality of catalyst particles are chemisorbed bi-metallic particles derived from platinum and ruthenium precursors.

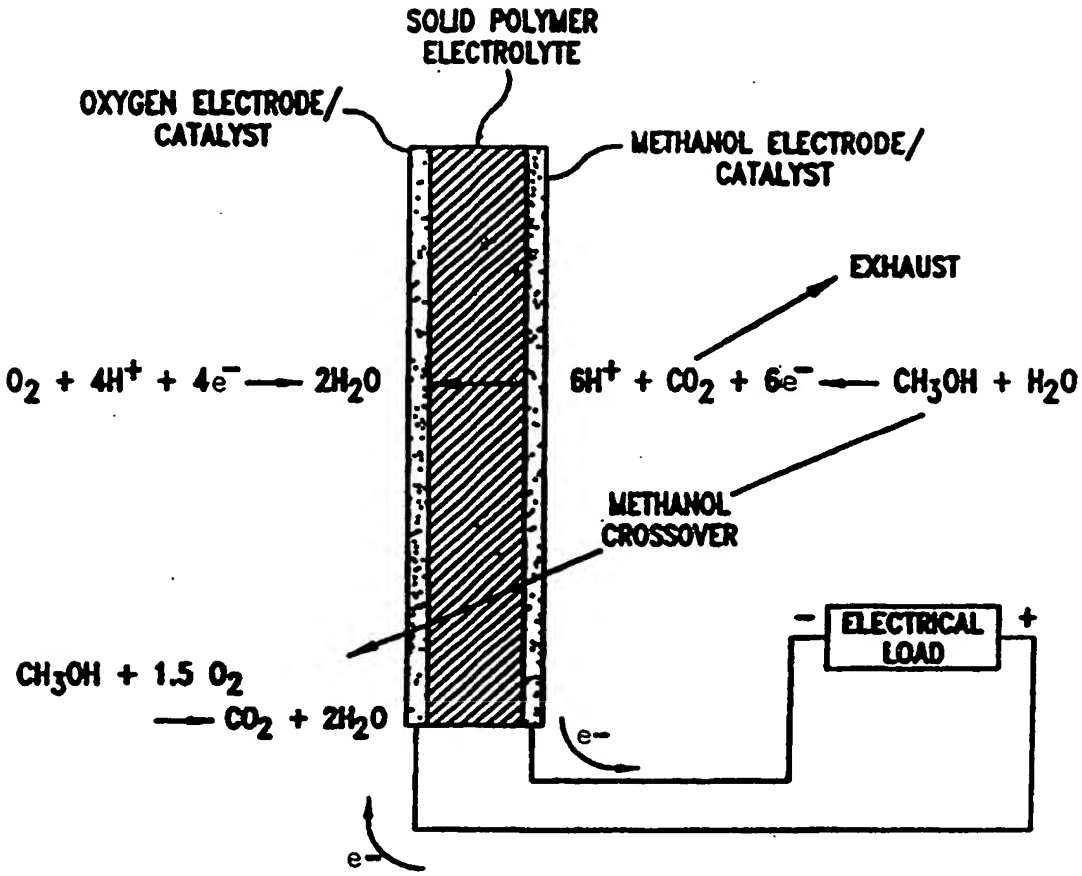


FIG. 1
PRIOR ART

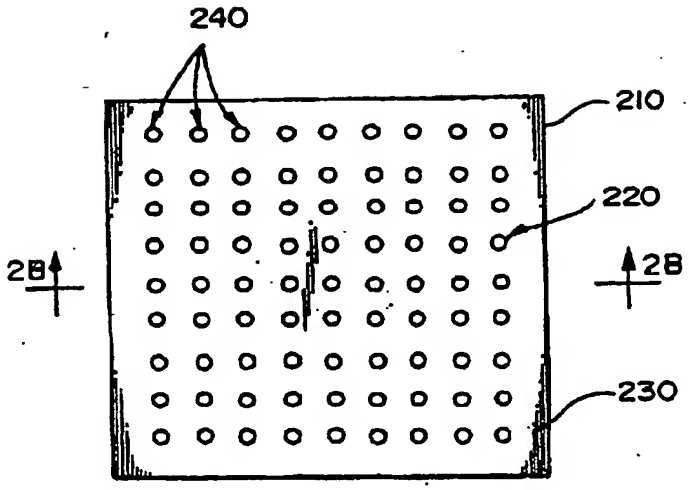


FIG. 2A

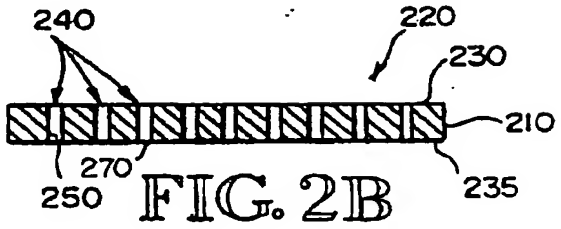


FIG. 2B

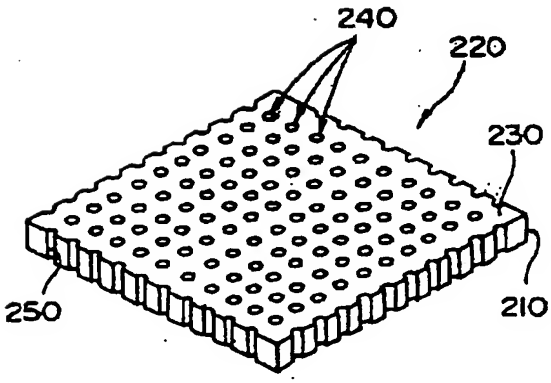


FIG. 2C

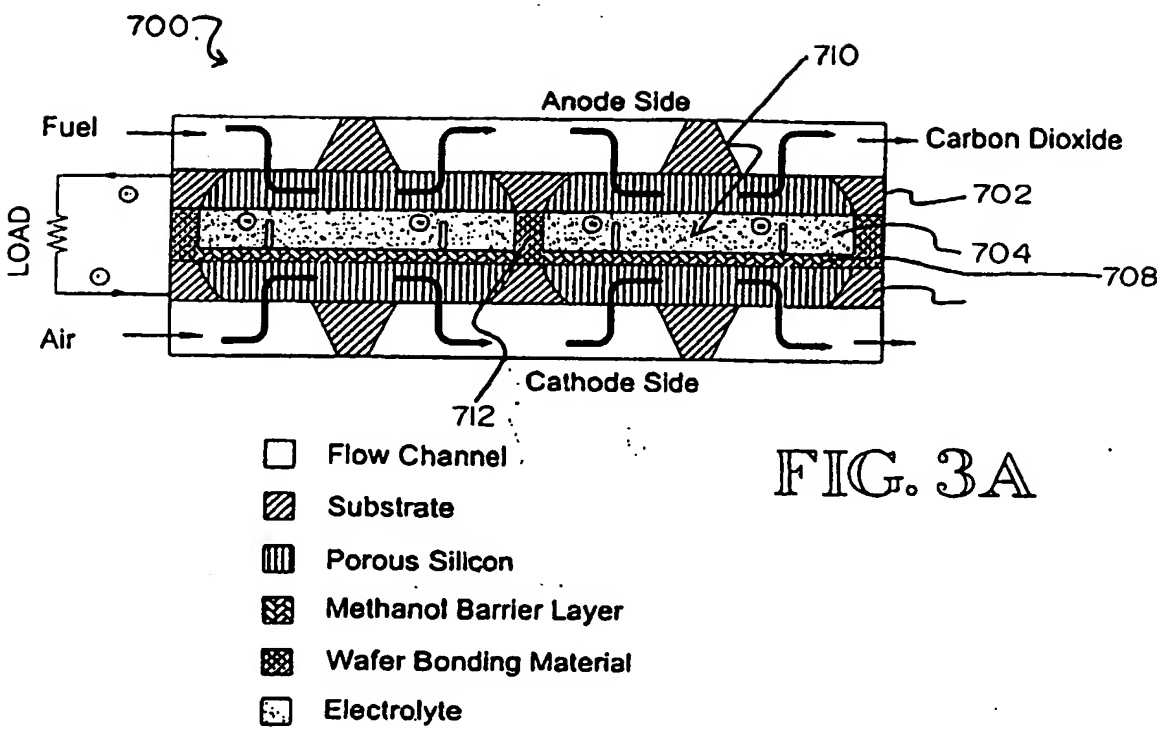

700
710
Anode Side
Fuel
Carbon Dioxide
LOAD
702
704
708
Air
Cathode Side
712
Flow Channel
Substrate
Porous Silicon
Methanol Barrier Layer
Wafer Bonding Material
Electrolyte

FIG. 3A

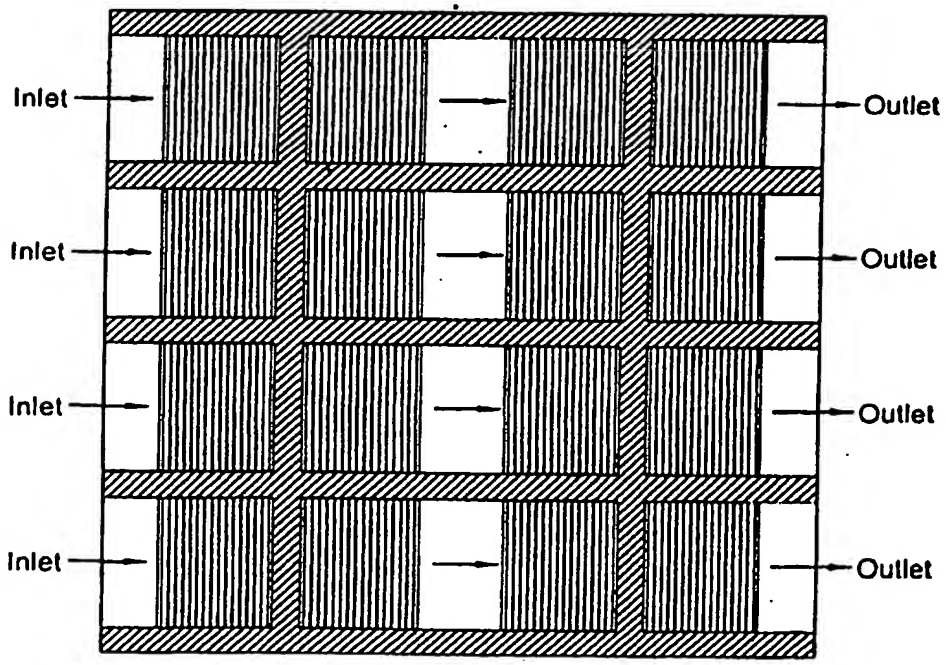
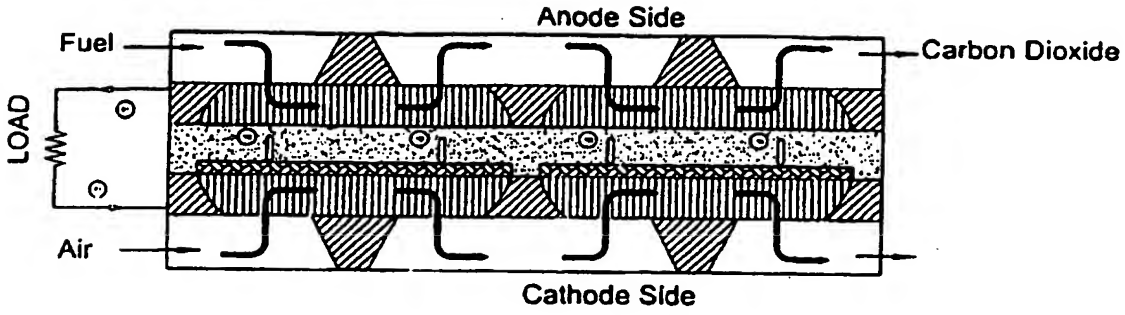

Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

FIG. 3B


Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Cathode Side

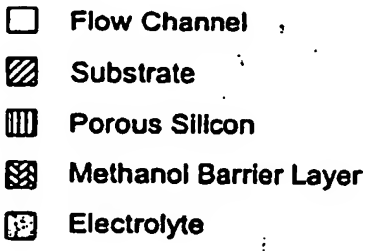
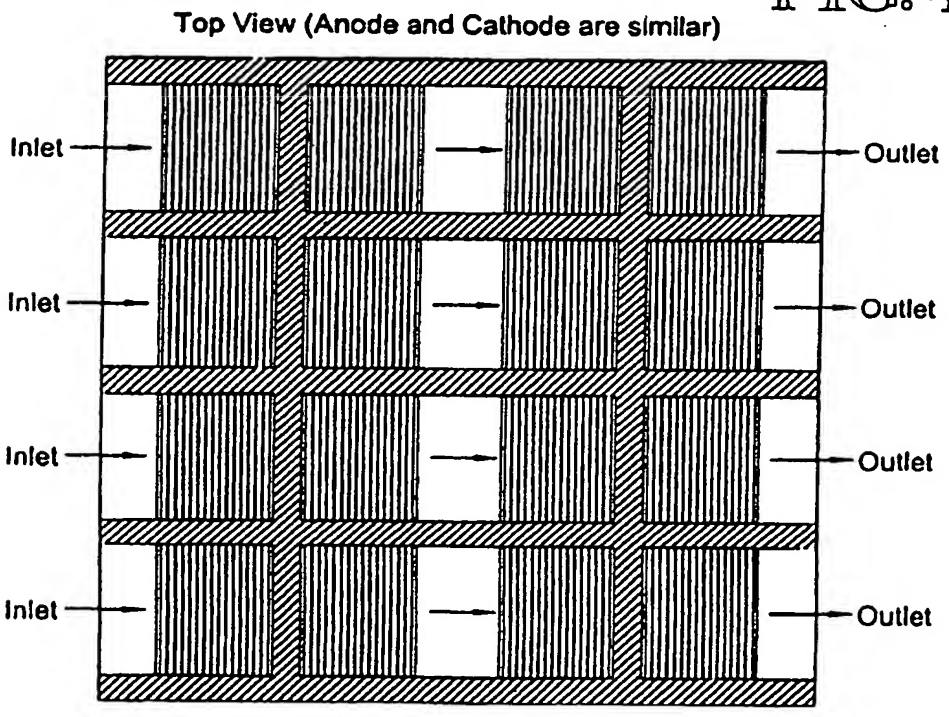

Flow Channel
Substrate
Porous Silicon
Methanol Barrier Layer
Electrolyte

FIG. 4A

FIG. 4B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

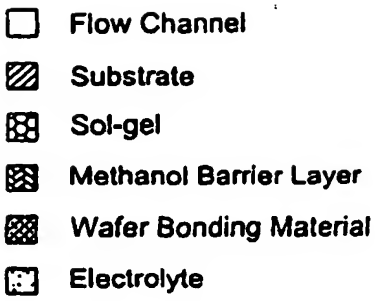

Flow Channel
Substrate
Sol-gel
Methanol Barrier Layer
Wafer Bonding Material
Electrolyte

FIG. 5A

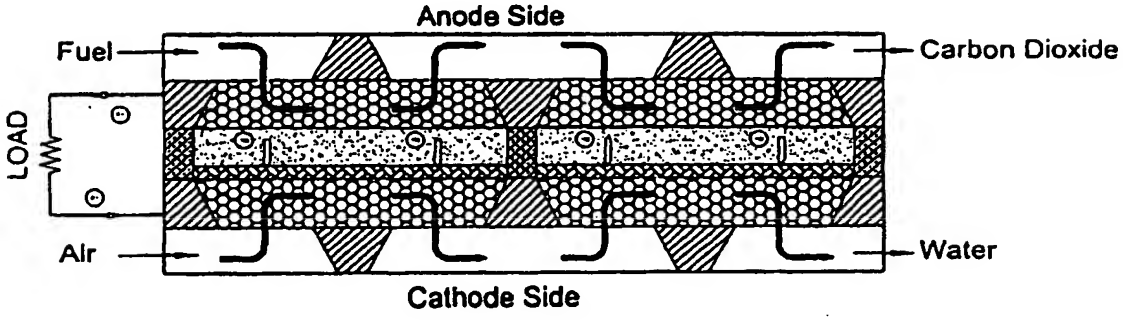
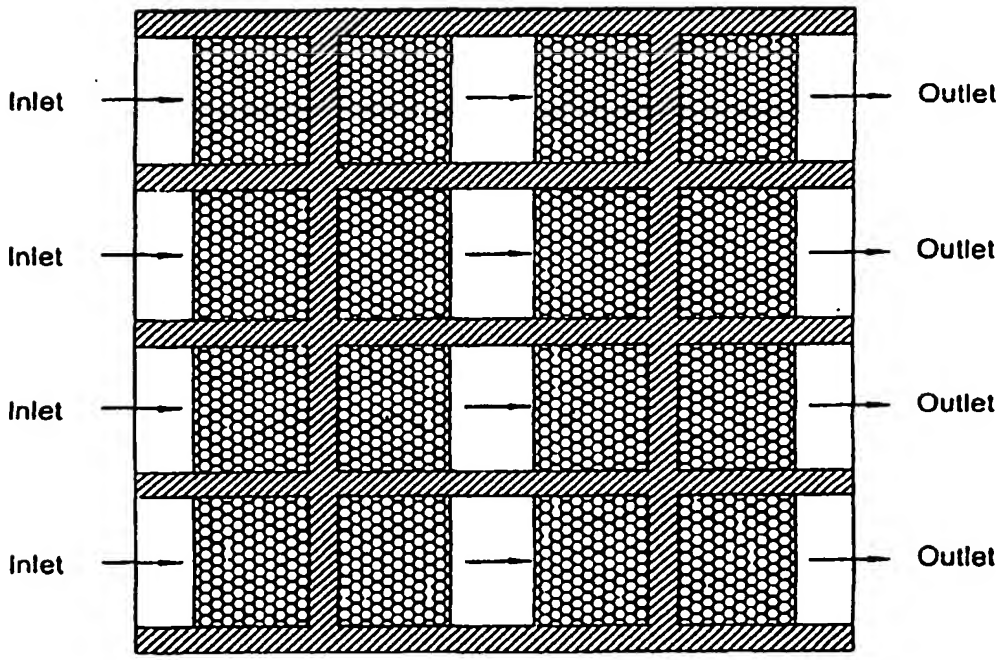

Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Water
Cathode Side

FIG. 5B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

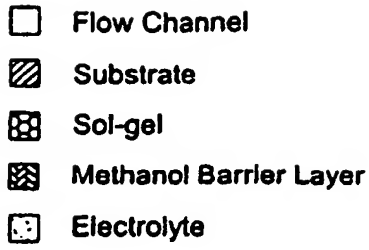

Flow Channel
Substrate
Sol-gel
Methanol Barrier Layer
Electrolyte

FIG. 6A

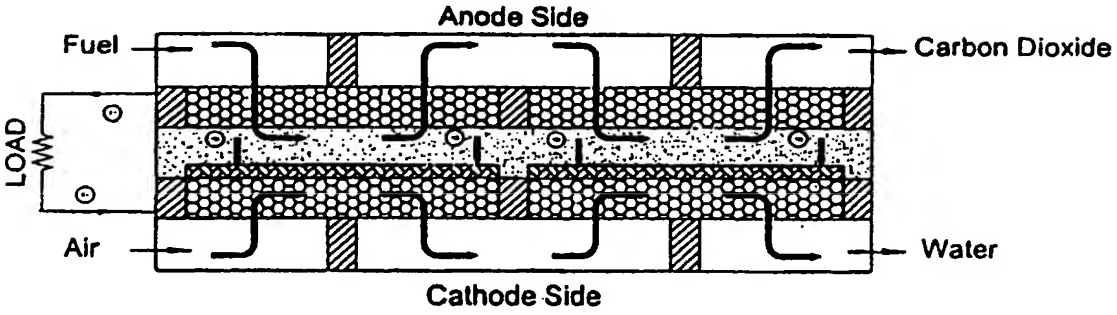
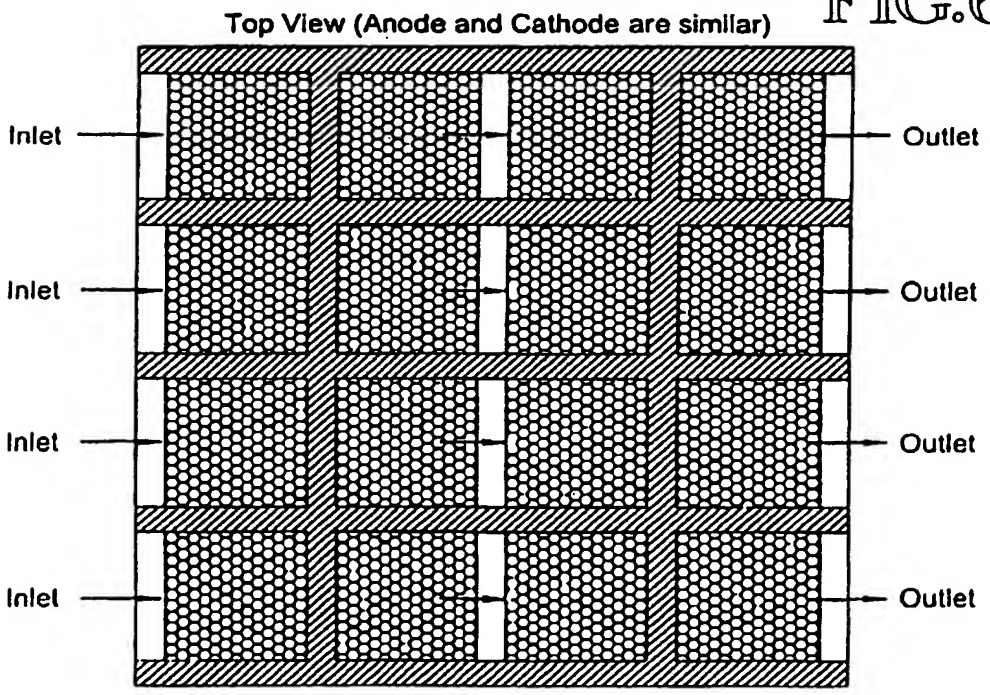

Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Water
Cathode Side

FIG. 6B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

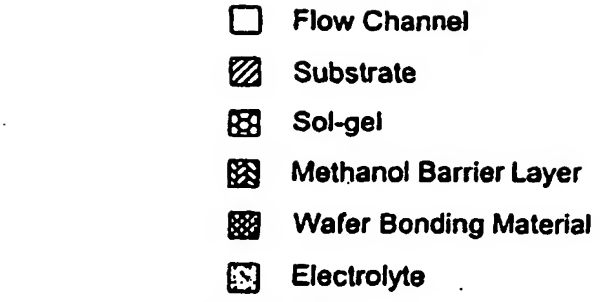

Flow Channel
Substrate
Sol-gel
Methanol Barrier Layer
Wafer Bonding Material
Electrolyte

FIG. 7A

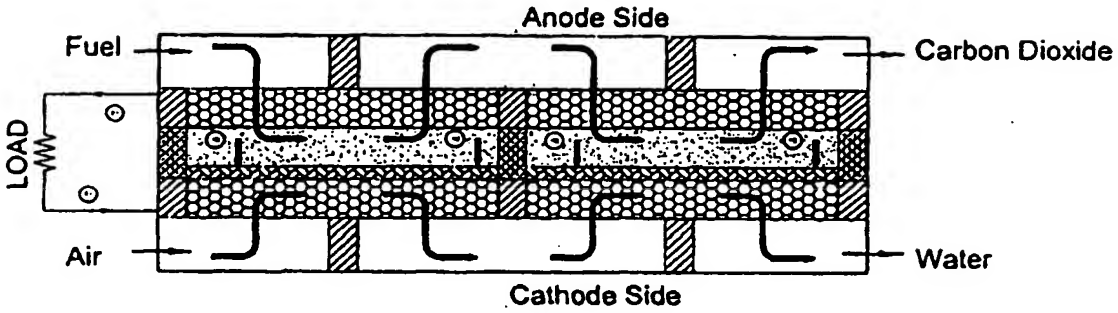
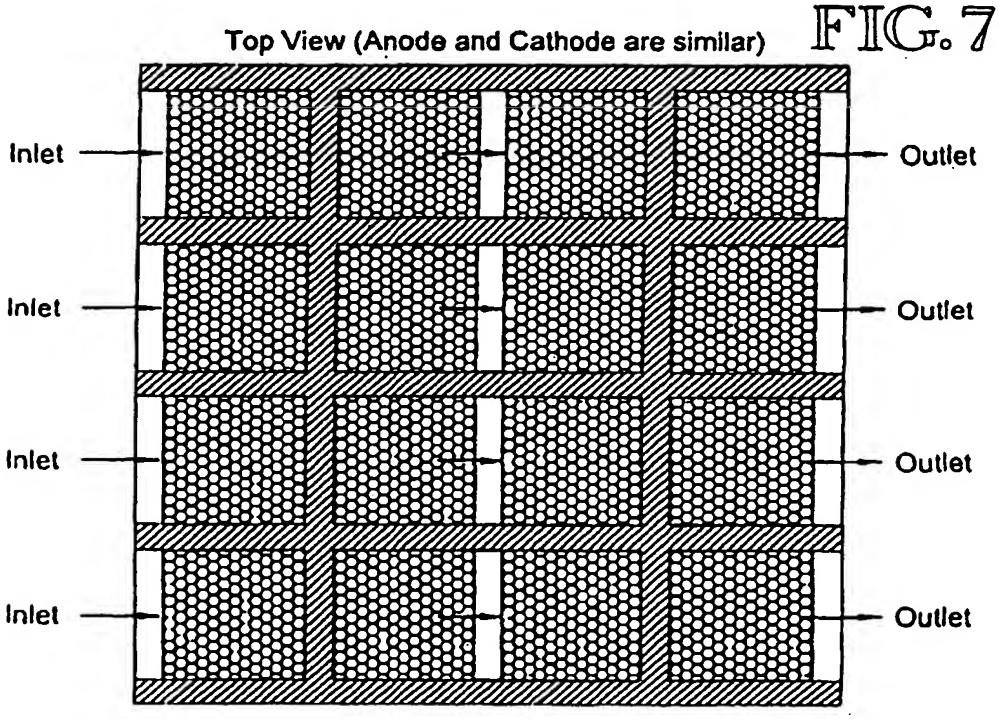

Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Water
Cathode Side

FIG. 7B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

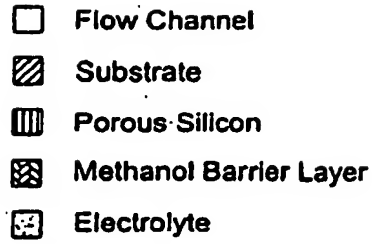

Flow Channel
Substrate
Porous Silicon
Methanol Barrier Layer
Electrolyte

FIG. 8A

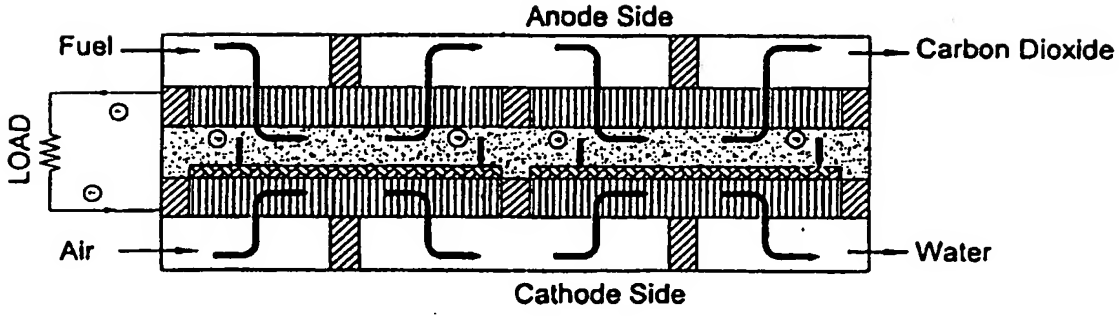
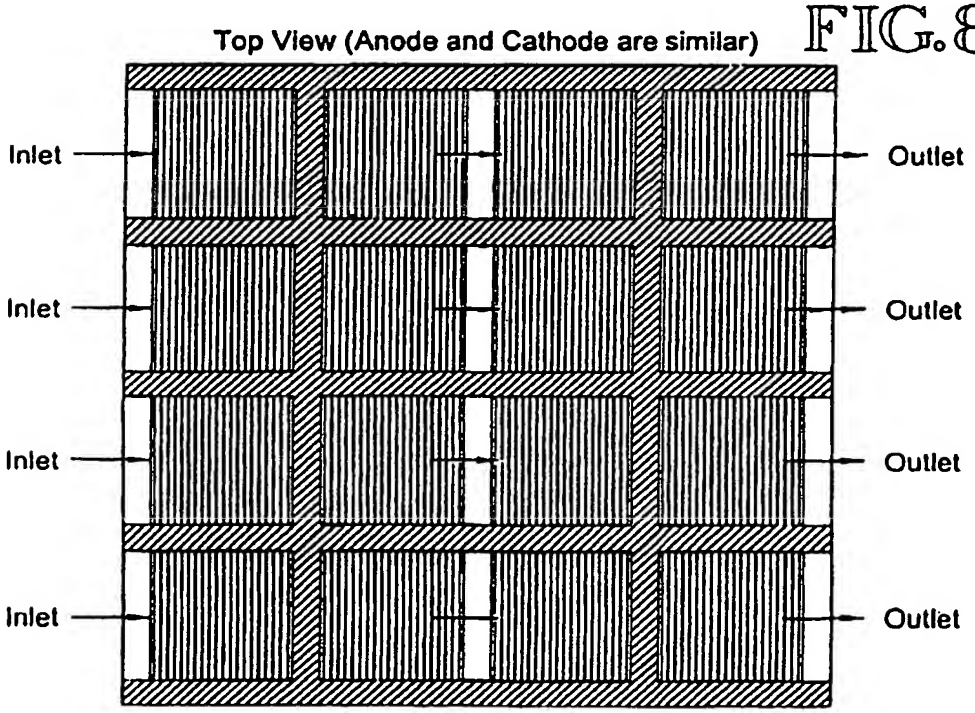

Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Water
Cathode Side

FIG. 8B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

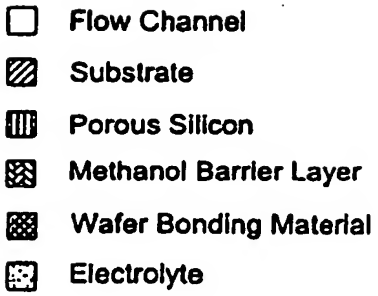

Flow Channel
Substrate
Porous Silicon
Methanol Barrier Layer
Wafer Bonding Material
Electrolyte

FIG. 9A

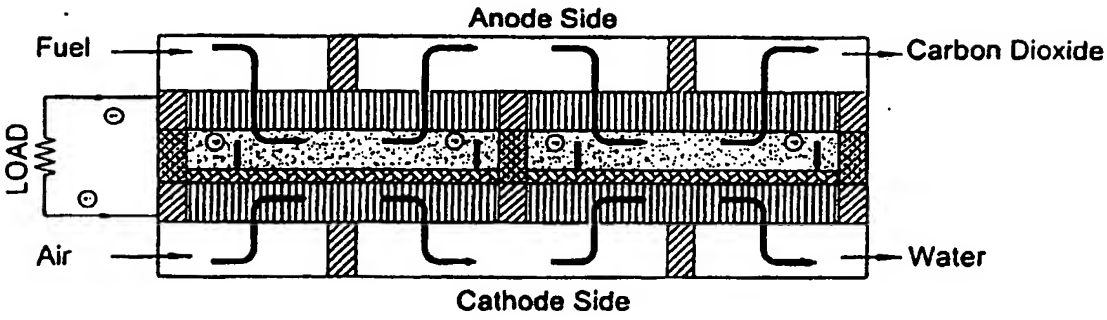
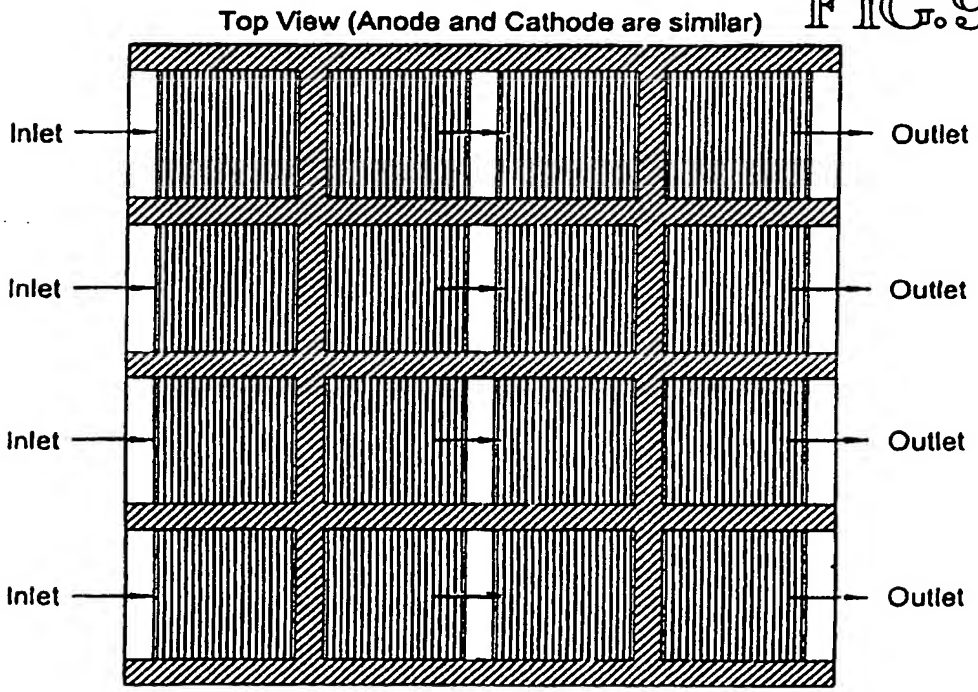

Anode Side
Fuel
Carbon Dioxide
LOAD
Air
Water
Cathode Side

FIG. 9B


Top View (Anode and Cathode are similar)
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet
Inlet
Outlet

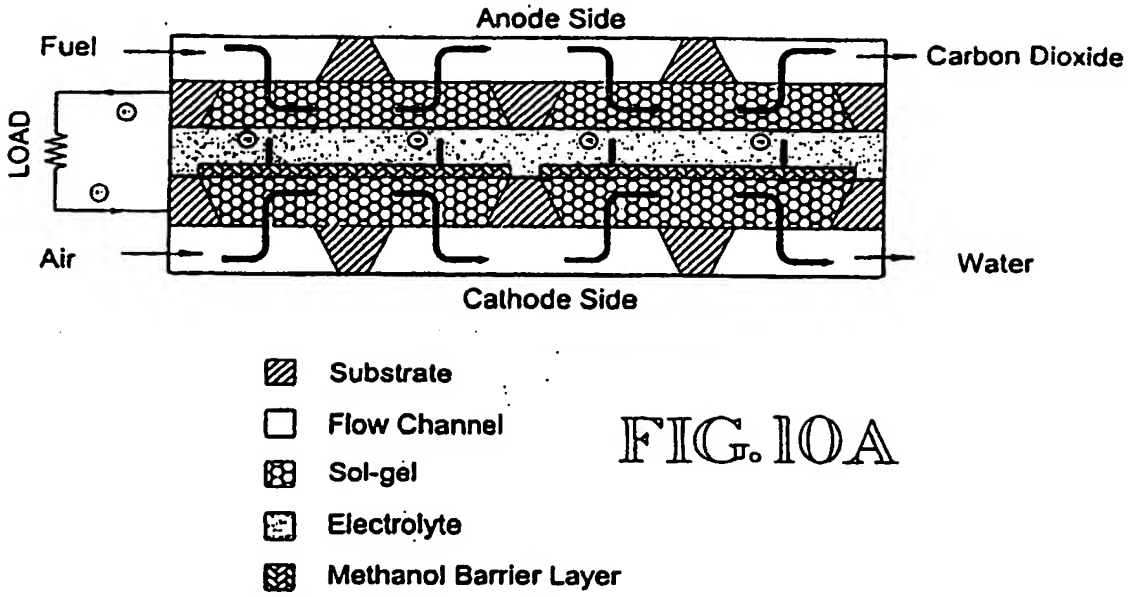
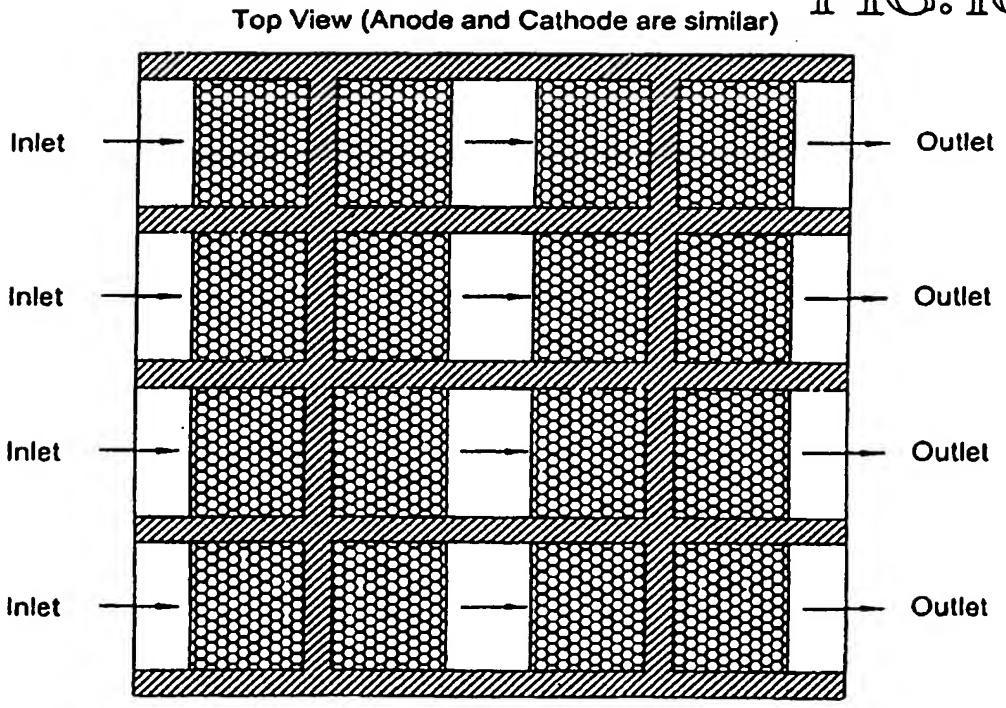


FIG. 10A

FIG. 10B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/12386

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : H01M 4/86, 4/90, 4/92, 8/02, 8/04
US CL : 429/39, 40, 41, 44, 46
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 429/30, 32, 34, 39, 40, 41, 44, 46

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 197 57 320 A1 (FORSCHUNGSZENTRUM JUELICH GMBH) 01 July 1999, see abstract.	1
Y	US 5,262,021 A (LEHMANN et al) 16 November 1993, see column 1, lines 9-14 and 37-54; Figure 1.	1
Y	US 5,607,785 A (TOZAWA et al) 04 March 1997, see Figure 5.	1
Y, P	US 2002/0022570 A1 (REYNOLDS III et al) 21 February 2002, see the Figures; paragraph [0013].	1, 16-18, 20-25
Y	US 5,874,182 A (WILKINSON et al) 23 February 1999, see column 8, lines 8-25.	2-6
Y	WO 98/21777 A (FORSCHUNGSZENTRUM JUELICH GMBH) 22 May 1998, see the abstract.	7-10
Y	US 5,961,887 A (ZHENG et al) 05 October 1999, see column 3, lines 4 and 43.	12-14
Y	US 5,523,177 A (KOSEK et al) 04 June 1996, see the abstract.	13, 14
Y	FR 2667728 A1 (SORAPEC) 10 April 1992, see abstract; Figure 1.	24, 25

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
21 June 2002 (21.06.2002)

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/12386

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 199 14 681 A1 (MULLER et al) 05 October 2000, see the abstract.	1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/12386

Continuation of B. FIELDS SEARCHED Item3:

USPT, US-PGPUB, EPO, JPO, Derwent

search terms: silicon, si, substrate, perforat*, hole, opening, sol gel, solgel, catalyst, surface, pore, porous, platinum, ruthenium, oxide, methanol